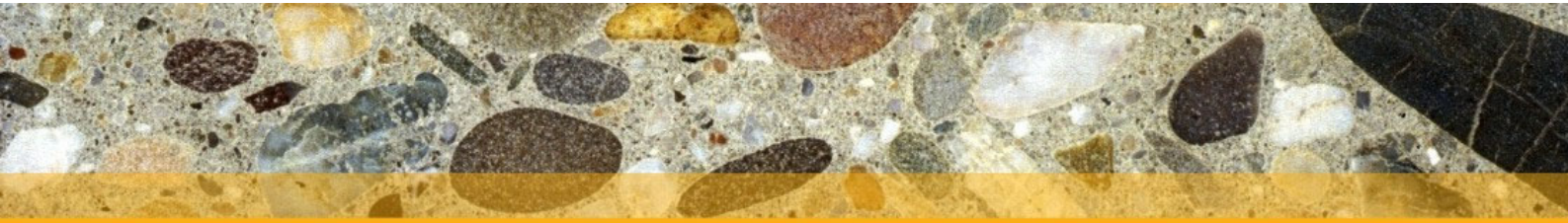




ecra

european cement research academy



Newsletter 5/2003

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Next seminars and workshops to come:

- Limitation of Sulphur and Chloride Cycles Using Bypass Systems
September, 30, 2003
- Plant Examinations
December 2-4, 2003

For details see: <http://www.ecra-online.org>

Ecra stands its ground after first year's halftime

23 members have joined the Academy – Participants are from all over the world

More than 6 months after its foundation, the European Cement Research Academy draws a positive conclusion from the first set of seminars and workshops, which have taken place so far. Participants from the member companies and member associations have taken advantage from this new forum for research exchange. In November, the Technical Advisory Board will finalise the programme for the year 2004.

The seminars and workshops, which have taken place so far focused on process technology and environmental issues. In addition a seminar on the interaction between cement and concrete admixture was held. The participants have pointed out that they especially appreciate to have sufficient time for exchange and discussion. Each seminar and each workshop started with a dinner the night before. This allowed the participants to come easily into contact and to exchange their specific views and experiences which they had gained in their own companies.

The feedback from the participants was carefully evaluated by the management. It turned out that the information given in the seminars and workshops was highly appreciated. In order to further improve the exchange of research results participants are encouraged to send specific questions or points of common interest prior to the events.

This allows to focus on specific demands and wishes of the participants as much as possible by taking into account their own specific situation.

At its November meeting the Technical Advisory Board will schedule the seminars and workshops for next year. The members of the Academy are always encouraged to make suggestions for new issues to be communicated and discussed. The ecra has received a couple of ideas for the future issues and will certainly prepare an interesting programme for next year.

The ecra web site is increasingly used by participants and representatives of member companies and associations to gain information on the various subjects. Also the web site is used to a growing extent as a communication platform for the various events.

Table 1: The Members of the European Cement Research Academy

Aalborg Portland
Anneliese Zementwerke
Australian Cement Holdings
Buzzi Unicem
Cemex Trademarks Worldwide
cemuisse
Ciments Luxembourgeois
CRH
Dyckerhoff
HeidelbergCement Group
Hellenic Cement Industry
Association
Italcementi Group
jura cement
Lafarge CTEC
Nesher Israel Cement Enterprises
Portland Cement Association
Portlandzementwerk Wittekind
Povazská Cementären
Rohrbach Zement
Schwenk Zement
Titan Cement Company
Verein Deutscher Zementwerke
Wietersdorfer & Peggauer
Zementwerke

Avoiding damage as a result of alkali-silica reaction

A performance test for ASR should be developed

Some natural aggregates contain soluble silica which reacts with the alkalis of the pore solution in the concrete to form an alkali silica gel. This gel can swell if exposed to water and can cause damage to the concrete by expansion. The setting off and the course of a harmful alkali-silica-reaction (ASR) are dependent upon the type, reactivity, quantity and particle size distribution of the alkali-sensitive constituents, as well as on the effective alkali content in the pore solution and the moisture supply in the concrete.

The active alkalis in concrete originate from cement, admixtures and concrete additions and in some few cases even from aggregates. The main cement constituents and concrete additions influence the alkali regime in different ways. Therefore several investigations of the Research Institute focused on the question about the extent to which cement constituents and concrete additions contribute to the active alkalis in the pore solution.

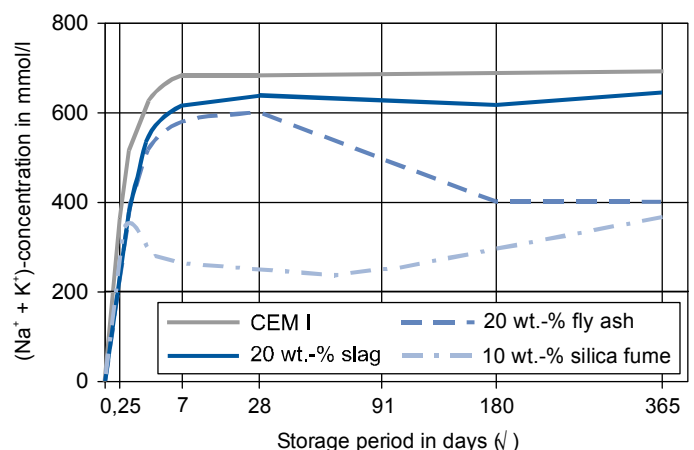
Pore solutions

The pore solution of hardened cement paste and concrete was examined as a function of the age of hydration (Fig. 1). Evaluation of the

material balances showed that blast furnace slags only make an insignificant contribution of alkalis to the pore solutions, so that there is a decrease in the available alkali con-

centration, which is virtually proportional to the amount of clinker replaced. Fly ash exhibits a similar behaviour up to a hydration age of 28 days, but beyond that it fixes alkalis in the

Fig. 1: Influence of 20 wt.-% fly ash or slag and 10 wt.-% silica fume on the alkali concentration of the pore solution



reaction products as the hydration progresses. Even greater fixation occurs at a very early age with the use of silica fume. Here it is apparent, however, that this fixation is not permanently stable. Some of the initially combined alkalis are released again with increasing hydration time.

For more extensive interpretation of the dissolving and fixing mechanisms it is necessary to locate the position of the alkalis in the hardened cement paste.

Pozzolanic additions

In contrast to the pore solution investigations, the results from long-term tests on concrete specimen with gravel, which contained opaline sandstone and flint as alkali sensitive constituents, did not confirm the positive effect of silica fume. This turned out from an investigation for which a reference concrete containing 500 kg Portland cement with an Na_2O -equivalent of 1.3 wt.-% was produced. If 10 wt.-% of the cement was replaced by silica fume, the harmful effect of ASR was not reduced in specimens stored outside. The concrete bars demonstrated increased expansions (Fig. 2) and the cubes a marked crack formation. In contrast, concrete bars that were stored in the 40 °C-fog chamber, showed no expansion resulting from ASR. A crack formation on the

cubes in the fog chamber was not observed either. It has not yet been established to what extent the test conditions in the fog chamber contributed to a reduction of the effective alkalis when silica was used.

Furthermore it must be found out to what extent the results from the fog chamber investigations can be transferred to practical use when pozzolanic additions are used.

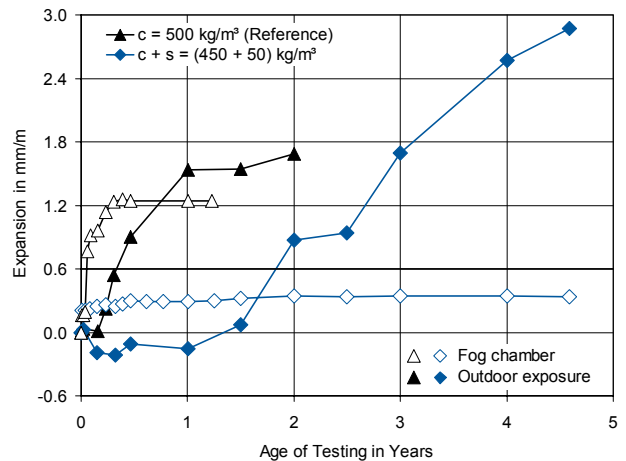
The PARTNER project

It was shown above that storing concrete prisms in a 40 °C-fog chamber is not the worst case for testing a harmful alkali-silica-reaction. Storing at an outdoor exposure site in Central Europe showed for some concrete mixes more damages. This is one of the reasons why some of the European cement companies and the Research Institute in Duesseldorf take

part in the European research programme "PARTNER" sponsored by the European Commission. This programme aims to classify alkali-sensitive aggregates from Europe in terms of their sensitivity to alkalis by using various test methods. In this process the suitability of existing methods is reviewed and the pertinent regulations are rendered more precise, if necessary.

Till now it is very difficult to examine whether concrete to be used in practice will suffer a harmful ASR. During the PARTNER project a test method used in France, which consists of storing concrete prisms at 60 °C and nearly 100 % relative humidity for 3 to 6 month is taken into consideration. This method could be established as ASR performance test for concrete. In the Research Institute this will be tested with different concrete compositions to be used in structures.

Fig. 2: Expansion of concrete beams in the 40 °C-fog chamber and at an outdoor exposure site (reference concrete and concrete with silica fume s)



Lowering the SO₂ emissions by controlling the sulphur cycles

Sulfite formation in the raw mill plays an important role when using the dry additive technique

The levels of SO₂ in the exhaust gases from rotary kilns in the cement industry are essentially attributable to the content of readily volatile sulphur compounds (pyrites, marcasite) in the raw materials used. The level of emissions therefore depends on the content of these readily volatile sulphur compounds in the particular deposit. Sulphur compounds form significant circulation systems in the kiln plant. Therefore, if SO₂ emissions have to be reduced effectively, in-depth knowledge about the behaviour of these compounds in the individual plant is essential.

The European BREF document for the cement industry specifies 200-400 mg SO₂/m³ as the associated emission level for sulphur dioxide which can be achieved with Best Available Techniques. Different BAT abatement techniques are used depending on the initial level of the SO₂ concentration. The dry additive process with the addition of hydrated lime to the kiln feed or preheater exit gas is designated in the BAT reference document for initial levels of SO₂ emission con-

centrations of 400-1200 mg/m³. Secondary processes, such as the wet scrubber are designated for starting levels significantly higher than 1200 mg/m³. The European Directive on the Incineration of Waste gives a SO₂ limit of 50 mg/m³ for cement kilns burning secondary fuels. Exemptions can be granted, if the SO₂ emissions derive from low volatile sulphur compounds in the raw material. Nevertheless, a limit of 50 mg/m³ is hard to be met for most cement kilns.

The Research Institute of the Cement Industry has investigated the material and process engineering parameters influencing SO₂ emissions for several years. The most recent industrial trials have furnished information on the behaviour of sulphur in the precalciner and in the external cycle of the kiln system.

Easily volatile sulphide (FeS₂) input into the preheater via the raw feed oxidises to form SO₂ in a temperature range of 300 to 500 °C. If

the SO_2 reacts with calcium, calcium sulphite (CaSO_3) is formed as an intermediate product, which in turn disproportionates to form calcium sulphide (CaS) and calcium sulphate (CaSO_4) at about 600°C . At the operating conditions prevailing in the preheater, calcium sulphide is decomposed to form SO_2 . Part of the SO_2 thus formed is bound directly by the kiln feed in the upper cyclone stages. During mill-on operation, a considerable portion is bound in the drying and grinding plant. When the precipitated reaction products re-enter the burning process with the kiln meal, the external recirculating sulphur system is closed.

Fig. 1 shows a concentration profile of the sulphur compounds sulphate, sulphide and sulphite contained in the kiln feed that illustrates the processes inside the cyclone preheater. The kiln feed contained about 0.24 wt.-% sulphate, 0.38 wt.-% sulphide and 0.05 wt.-% sulphite (all given in wt.-% SO_3). The sulphide input is converted completely in the first and second cyclone stages. A small quantity of sulphite was found in the kiln feed below the first cyclone stage. A further portion is formed when SO_2 reacts with the kiln meal. The sulphate content of the meal increases owing to the reaction of SO_2 with the kiln meal and the sulphite turnover in this area. The sulphate contents measured in the hot meals below the third cyclone stage were considerably higher. They are indicative of a marked internal recirculating sulphur system between the sintering zone of the rotary kiln and the lower preheater stages.

Kiln operation in interconnection with drying and grinding constitutes a very effective primary SO_2 abatement measure. Industrial trials show that

Fig. 1: Concentration profile of different sulphur compounds in a cyclone preheater

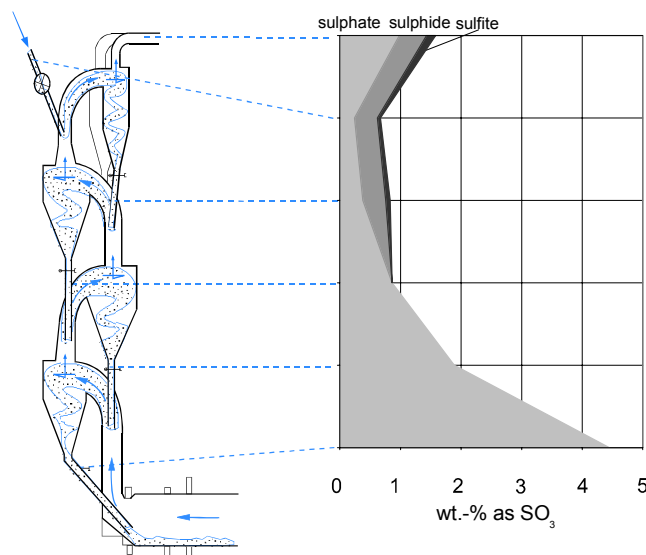
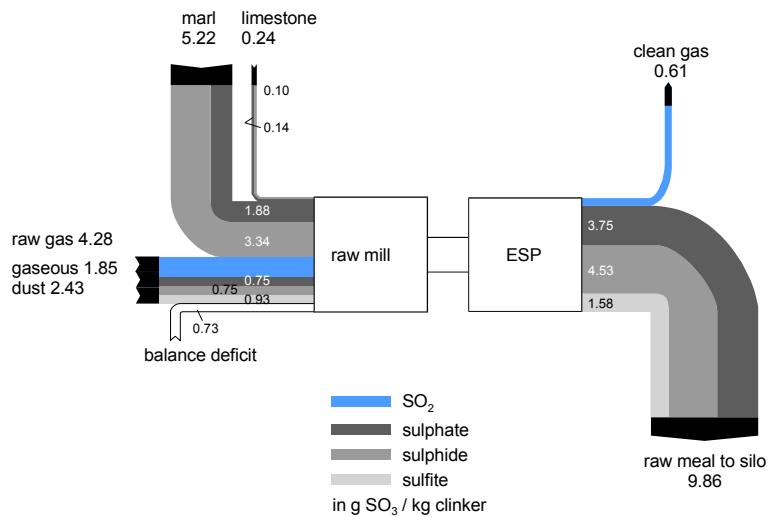


Fig. 2: Differentiated sulphur mass balance of a raw mill with downstream gas cleaning



SO_2 binding rates in the raw mill range between 40 and 75 %. Most of the sulphur reactions in the external recirculating system become intelligible from the differentiated sulphur mass balance of a vertical roller mill with downstream gas cleaning shown in **Fig. 2**. Lime hydrate was added to the exhaust gas to reduce SO_2 during the trial. The mass balance inputs consist of the raw materials marl and limestone fed the mill. In addition to that, exhaust gas including dust enters the mill for drying. The outputs consist of the final product (ground raw material) and the clean gas.

The mass balance shows that, at $5.22 \text{ g SO}_3/\text{kg clinker}$ (S as SO_3), more than 50 wt.-% of the sulphur input into the mill occurs via the marl. Sulphide accounts for the largest portion, sulphate for a smaller one. Input via the limestone consists of $0.14 \text{ g SO}_3/\text{kg clinker}$ in the form of sulphate and $0.1 \text{ g SO}_3/\text{kg clinker}$ in the form of sulphide. As expected, the sulphite contents of the raw materials were within the range of the detection limit of the analysis method, which is 0.03 wt.-%. $1.85 \text{ g SO}_3/\text{kg clinker}$ enters the

mill as SO_2 via the raw gas; this corresponds to approx. 20 % of total input. Additional sulphur is input via the preheater exit gas dust, which is characterised by a higher sulphate and sulphite concentration than the kiln feed. At $2.43 \text{ g SO}_3/\text{kg clinker}$, the preheater exit gas dust accounts for about 25 wt.-% of sulphur input. What is striking about this input is that sulphite accounts for nearly 40 wt.-%. A possible reason for this is the fixation of the SO_2 in the exhaust gas by the lime hydrate, which, given the conditions prevailing, results in the formation not only of sulphate, but also of sulphite as a reaction or intermediate product. The mass balance further reveals that additional sulphite is formed in the raw mill. As the sulphate mass flow increases from 2.77 to $3.75 \text{ g SO}_3/\text{kg clinker}$ in the mill as well, one can proceed on the assumption that part of the sulphite formed during SO_2 fixation oxidises to form sulphate in the mill already. The possible reaction partners of the SO_2 are unconverted lime hydrate or calcium carbonate.

The sulphur output from the system occurs via the mill exhaust gas and the ground raw material. A mass flow of $0.61 \text{ g SO}_3/\text{kg clinker}$ is output via the mill exhaust gas. Most of the remaining sulphur is present in the ground raw material in the form of sulphate and sulphide, a smaller portion also in the form of sulphite. The rate of SO_2 binding at this plant was 67 % relative to SO_2 input via the exhaust gas from the preheater.

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